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(54) **METHOD FOR MAKING CURRENT COLLECTOR**

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(51) **Int. Cl.**

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H01M 2/00	(2006.01)
H01M 4/66	(2006.01)
H01G 11/68	(2013.01)
H01G 11/70	(2013.01)
H01G 11/84	(2013.01)
H01M 10/052	(2010.01)
H01G 11/28	(2013.01)

(52) **U.S. Cl.**

CPC ***H01M 2/00*** (2013.01); ***H01G 11/68*** (2013.01); ***H01G 11/70*** (2013.01); ***H01G 11/84*** (2013.01); ***H01M 4/663*** (2013.01); ***H01M 4/667*** (2013.01); *H01G 11/28* (2013.01); *H01M 10/052* (2013.01); *Y02E 60/13* (2013.01); *Y10T 29/49112* (2015.01)

(58) **Field of Classification Search**

CPC H01M 4/04; H01M 4/0404; H01M 4/663
USPC 29/623
See application file for complete search history.

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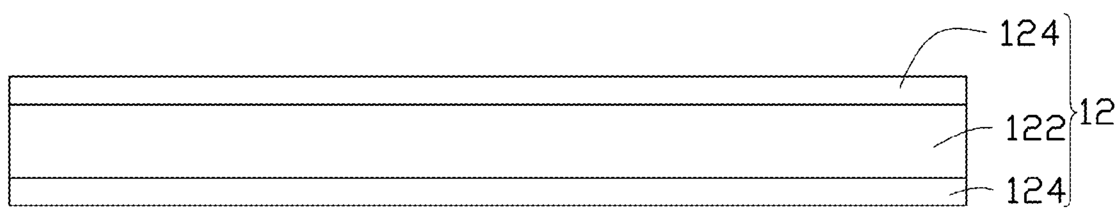
(57) **ABSTRACT**

A method for making current collector is described. In the method, a substrate, a graphene film, and a plastic support film are provided. The substrate has a surface. The graphene film is disposed on the surface of the substrate. The graphene film disposed on the surface of the substrate and the plastic support film are laminated to form a substrate-graphene-plastic support film composite structure. The substrate is removed.

11 Claims, 9 Drawing Sheets



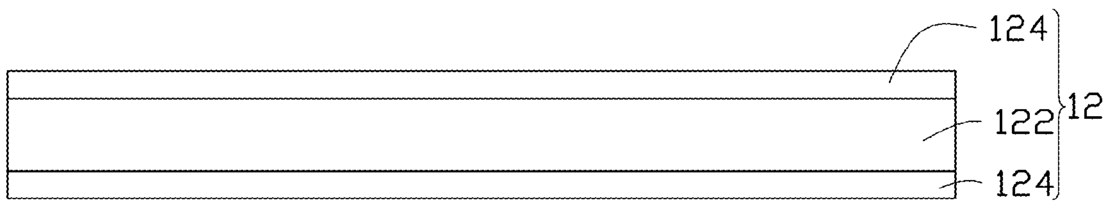


FIG. 1

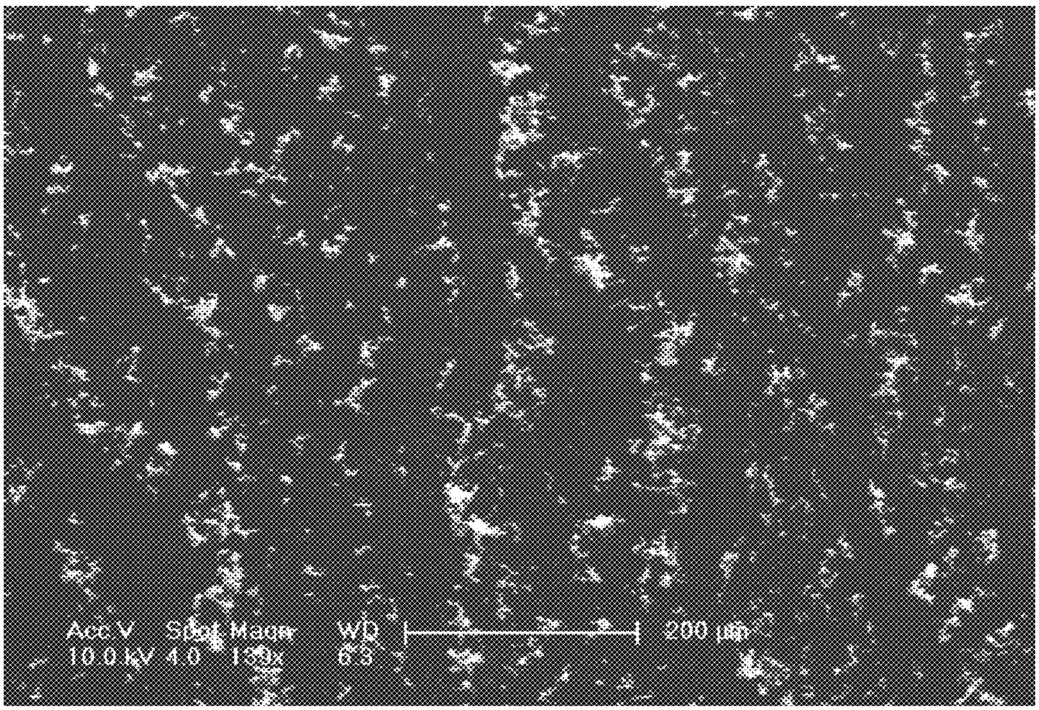


FIG. 2

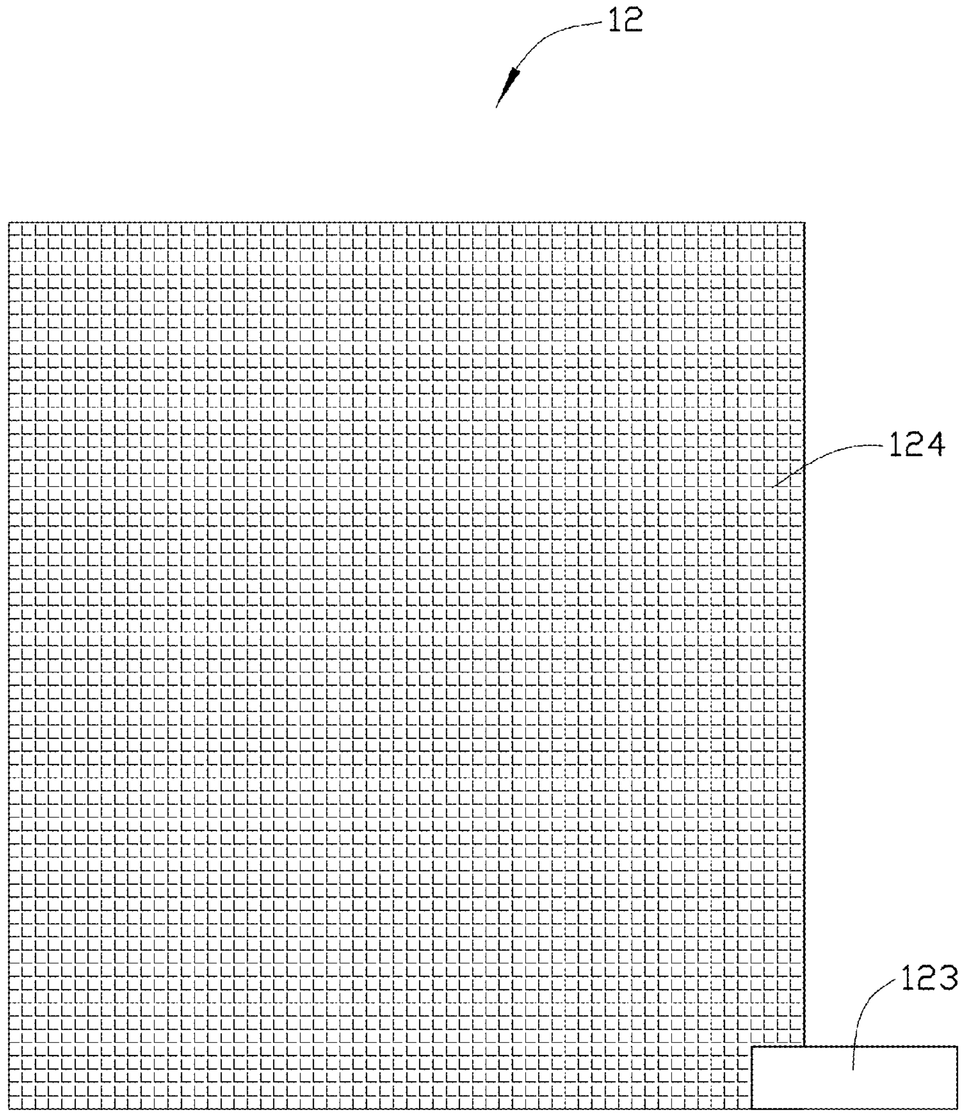


FIG. 3

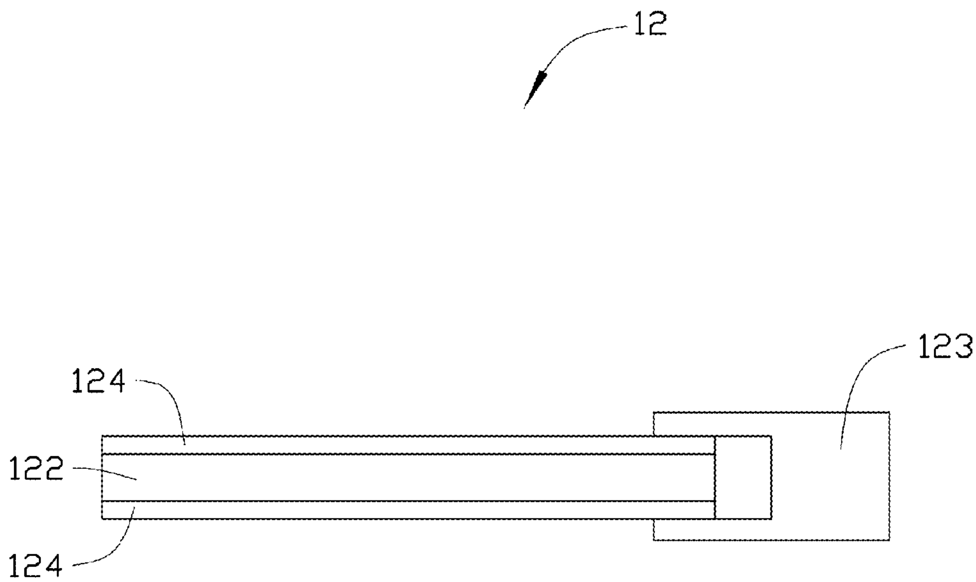


FIG. 4

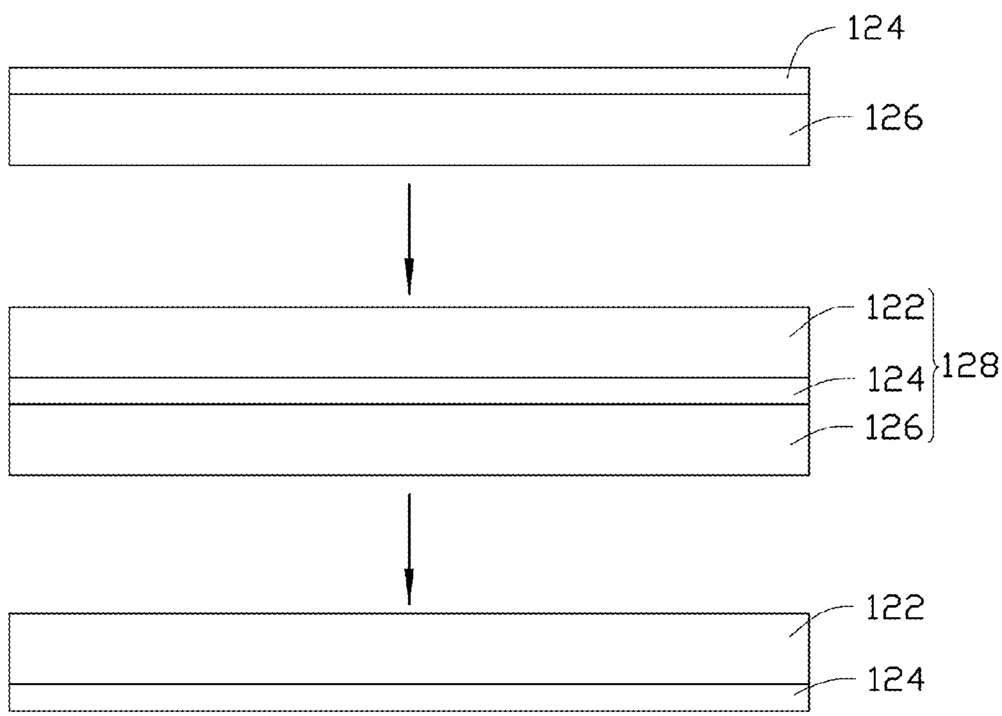


FIG. 5

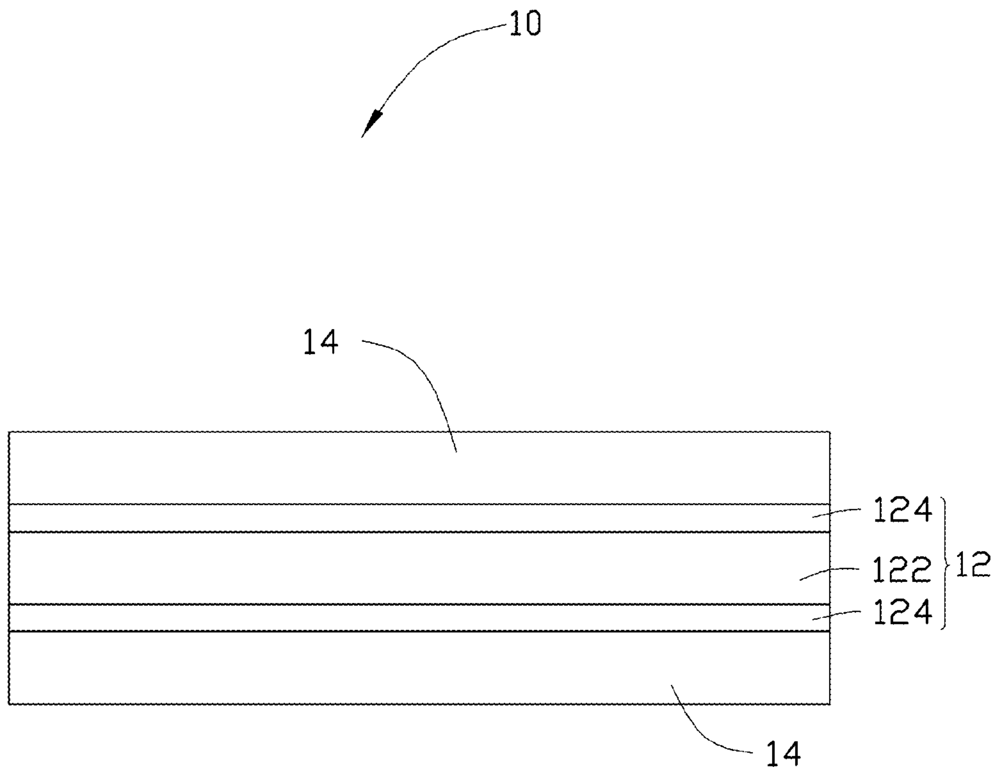


FIG. 6

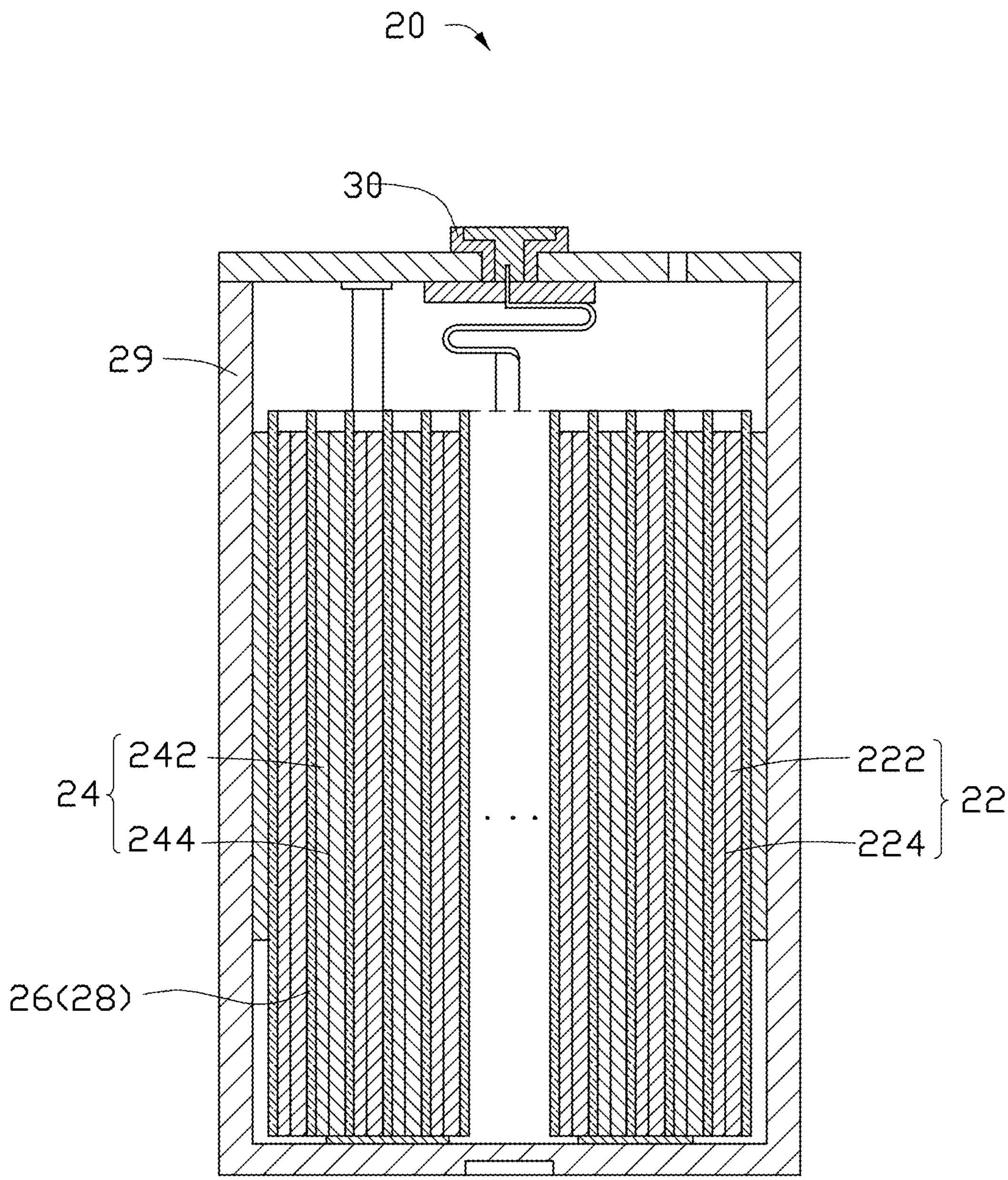


FIG. 7

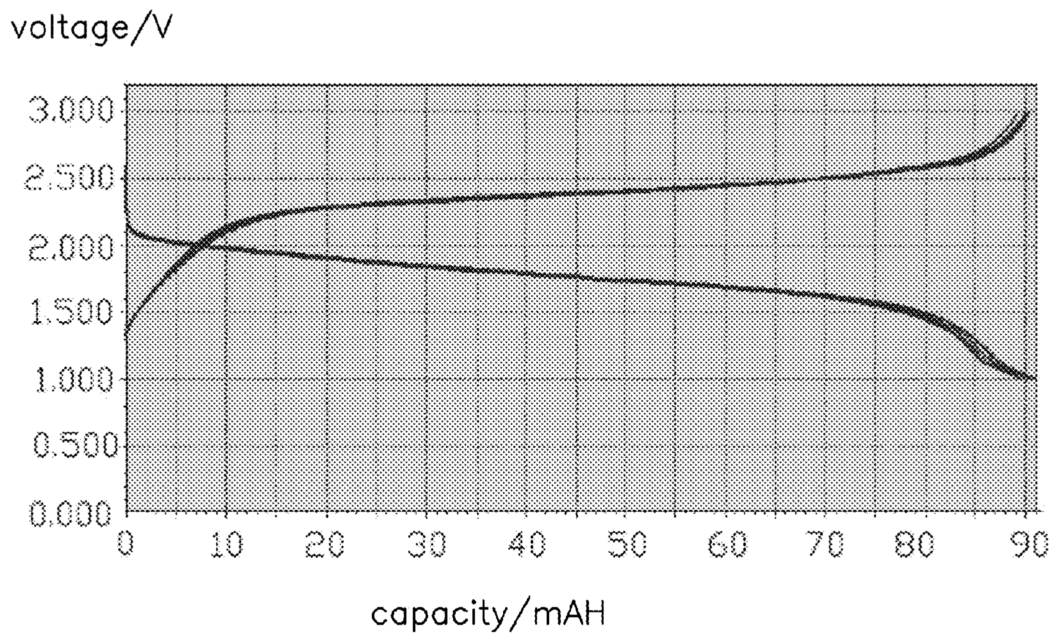

voltage/V
3.000
2.500
2.000
1.500
1.000
0.500
0.000
0
10
20
30
40
50
60
70
80
90
capacity/mAH

FIG. 8

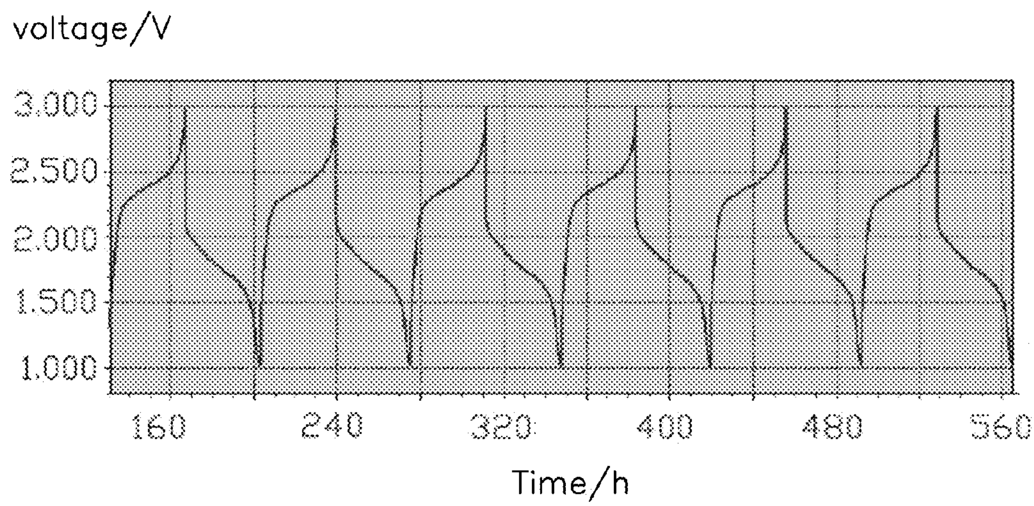

voltage/V
3.000
2.500
2.000
1.500
1.000
160
240
320
400
480
560
Time/h

FIG. 9

METHOD FOR MAKING CURRENT COLLECTOR

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims all benefits accruing under 35 U.S.C. §119 from China Patent Application No. 201210153299.5, filed on May 17, 2012, in the China Intellectual Property Office, the contents of which are hereby incorporated by reference. This application is related to common-assigned application entitled, "CURRENT COLLECTOR, ELECTROCHEMICAL CELL ELECTRODE AND ELECTROCHEMICAL CELL" filed Dec. 18, 2012, Ser. No. 13,717,837.

BACKGROUND

1. Technical Field

The present disclosure relates to a method for making a current collector.

2. Description of Related Art

Current collectors are the main components of electrochemical cells. The current collectors are used as electron transfer channels for transferring electrons formed in electrochemical reactions of the electrochemical cells to an external circuit to provide electric currents. Performances of the electrochemical cells are affected by the performances of the current collectors.

The current collectors are usually made of metal foils, such as copper and aluminum foils. The metal foils are usually heavy in weight, thus the energy density of the electrochemical cells may be decreased. In addition, the metal foils are prone to corrosion; therefore the life expectancy of the electrochemical cells may be decreased.

What is needed, therefore, is to provide a method for making a current collector, which has a small weight and an excellent corrosion resistant.

BRIEF DESCRIPTION OF THE DRAWING

Many aspects of the present disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, the emphasis instead being placed upon clearly illustrating the principles of the present embodiments.

FIG. **1** shows a schematic view of a graphene film coated on a plastic support film in one embodiment of a current collector.

FIG. **2** is a scanning electron microscopic (SEM) image of the graphene film coated on the plastic support film in the embodiment of the current collector of FIG. **1**.

FIG. **3** is a top view of one embodiment of the current collector of FIG. **1** comprising connector tabs.

FIG. **4** is a side view of one embodiment of the current collector of FIG. **1** comprising connector tabs.

FIG. **5** is one embodiment of a process of covering the graphene film on the plastic support film using a graphene transfer method.

FIG. **6** is a schematic view of one embodiment of an electrochemical cell electrode.

FIG. **7** is a schematic view of one embodiment of an electrochemical cell.

FIG. **8** is a test graph showing charge and discharge curves of one embodiment of a lithium ion battery.

FIG. **9** is a test graph showing charge and discharge cycling performance of the lithium ion battery of FIG. **8**.

DETAILED DESCRIPTION

The disclosure is illustrated by way of example and not by way of limitation in the figures of the accompanying drawings in which like references indicate similar elements. It should be noted that references to "another," "an," or "one" embodiment in this disclosure are not necessarily to the same embodiment, and such references mean at least one.

Referring to FIGS. **1** to **4**, one embodiment of a current collector **12** includes a plastic support film **122** and a graphene film **124** coated on at least one surface of a plastic support film **122**.

The plastic support film **122** can be a continuous sheet shaped film, network shaped film or porous shaped film. The plastic support film **122** can support the graphene film **124** and an electrode material layer. A thickness of the plastic support film **122** can be in a range from about 1 micron (μm) to about 200 μm. The plastic support film **122** can be a continuous and integrated film structure. A material of the plastic support film **122** can have a small density and a good resistance to the corrosion of an electrolyte solution. The material of the plastic support film **122** can be polyethylene, polypropylene, polrvinyl chloride, polystyrene or acrylonitrile-butadiene-styrene common polymer.

The graphene film **124** can be a continuous film structure and can continuously cover at least one surface of the plastic support film **122**. The graphene film **124** can directly contact the at least one surface of the plastic support film **122**. The graphene film **124** and the plastic support film **122** can be pressed together by a pressure, thus, the graphene film **124** and the plastic support film **122** can be compactly combined with each other by an intermolecular force. In addition, the graphene film **124** and the plastic support film **122** can be compactly adhered together by an adhesive. In one embodiment, the graphene film **124** covers on two opposite surfaces of the plastic support film **122** substantially perpendicular to a thickness direction of the plastic support film **122**. The graphene film **124** includes at least one graphene sheet. In one embodiment, the graphene film **124** includes a plurality of graphene sheets. The plurality of graphene sheets can be pieced together to form the graphene film **124** having a large area. The plurality of graphene sheets also can be stacked or overlapped with each other to form the graphene film **124** having a large thickness. The plurality of graphene sheets can be combined with each other by van der Waals attractive force. Each of the plurality of graphene sheets can include about one to ten layers of graphene. The graphene is a one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice. A thickness of the graphene film **124** can be in a range from about 0.8 nanometers (nm) to about 5 μm. In one embodiment, the thickness of the graphene film **124** is in a range from about 0.8 nm to about 1 μm. In addition, the graphene film **124** can consist of pure graphene. In another embodiment, the graphene film **124** consists of only one graphene having the thickness of about 0.8 nm. The graphene can fully cover the surface of the plastic support film **122**. In another embodiment, the graphene film **124** is composed of a plurality of graphene sheets having a thickness of 50 nm. The graphene has an excellent conductivity. A movement velocity of electrons in the graphene can reach to about 1/300 of a velocity of light which is much larger than the movement velocity of the electrons in other conductors. In addition, the graphene sheet has a large specific surface energy itself and can firmly combine with the plastic support film **122** and the electrode material layer by intermolecular force. Therefore, conductivity and electrochemical stability of the current collector **12** can be increased by covering the graphene film **124** on the surface of the plastic support film **122**.

The current collector **12** can further include a connector tab **123** used to electrically connect with an external circuit. The connector tab **123** can be in contact with the graphene film **124** and protrude from the graphene film **124** and the plastic support film **122**. Referring to FIG. **3**, in one embodiment, the connector tab **123** is a conductive sheet having a narrow strip shape, the graphene film **124** covers on one surface of the plastic support film **122**, and the connector tab **123** is directly disposed on the surface of the graphene film **124**. Referring to FIG. **4**, in another embodiment, the connector tab **123** is a "U" shaped conductor having two sheet shaped branches. Two opposite surfaces of the plastic support film **122** are covered by the graphene films **124**. One branch of the connector tab **123** is disposed on one surface of the graphene film **124**, and another branch of the connector tab **123** is disposed on another opposite surface of the graphene film **124**. Thus, the connector tab **123** can be electrically connected with two graphene films **124** disposed on two opposite surfaces of the plastic support films **122**. The connector tabs **123** can be adhered on the surfaces of the graphene film **124** by a conductive adhesive. A material of the connector tabs **123** can be a conductive material such as metal (e.g. copper or gold).

The current collector **12** can be fabricated by a solution coating method or a graphene transfer method. The graphene film **124**, disposing on the plastic support film **122**, having a large area or a large thickness can be fabricated by the solution coating method. The graphene film **124**, disposing on the plastic support film **122**, composed of a monolayer, continuous, and integrated graphene sheet can be fabricated by the graphene transfer method.

In one embodiment, the solution coating method for making the current collector **12** includes the following steps:

S**1**, providing a plurality of graphene sheets in powder form and dispersing the plurality of graphene sheets in a volatile solvent to form a graphene dispersion;

S**2**, coating the graphene dispersion on at least one surface of the plastic support film **122** to form a coating layer;

S**3**, removing the volatile solvent in the coating layer to form the graphene film **124**.

In the step S**1**, the plurality of graphene sheets can be fabricated by a mechanical exfoliation method, oxidation-reduction method, or chemical vapor deposition method. The volatile solvent can be an organic solvent or water. The organic solvent can be at least one of ethanol, acetone, ether, and chloroform. The graphene dispersion can be stirred to make the plurality of graphene sheets uniformly dispersed in the volatile solvent. The stirring method can be at least one of magnetically stirring, mechanical stirring, and ultrasonically vibrating. A mass percentage of the plurality of graphene sheets to the graphene dispersion can be in a range from about 0.05 wt % to about 5 wt %. The larger the mass percentage of the graphene dispersion, the thicker the graphene film **124**.

In the step S**2**, the coating method can be knife coating, brushing, spraying, electrostatic coating, roll coating, screen printing, or dip coating. In one embodiment, the graphene dispersion is dip coated on the surface of the plastic support film **122**. The dip coating includes the steps of completely dipping the plastic support film **122** in the graphene dispersion, and then lifting the plastic support film **122** out from the graphene dispersion. A dipping time period can be in a range from about 30 seconds to about 5 minutes. A lifting speed can be in a range from about 1 centimeter per minute (1 cm/min) to about 20 cm/min. In one embodiment, the dipping time period is about 2 minutes, and the lifting speed is about 10 cm/min. Under an adhesion force and gravity of the graphene dispersion, the surface of the plastic support film **122** can be continuously coated with a graphene dispersion film during the lifting process. The graphene dispersion film has a uniform thickness. In addition, the steps of dipping and lifting can be repeated several times or the concentration of the graphene dispersion can be adjusted to control the thickness and uniformity of the coating layer.

In step S**3**, the volatile solvent can be removed by drying in a high temperature or in room temperature. The graphene can be firmly adhered on the surface of the plastic support film **122** due to a surface tension of the volatile solvent and specific surface energy of the graphene sheet. Therefore, a dense and continuous graphene film **124** can be formed on the surface of the plastic support film **122**.

Referring to FIG. **5**, the graphene transfer method for making the current collector **12** includes the following steps:

M**1**, providing a substrate **126** having a surface and disposing the graphene film **124** on the surface of the substrate **126**;

M**2**, laminating the graphene film **126** disposed on the surface of the substrate **126** and the plastic support film **122** to form a substrate-graphene-plastic support film composite structure (SGPC) **128**; and

M**3**, removing the substrate **126**.

In the step M**1**, a material of the substrate **126** can be metal or nonmetal. The metal can be copper or nickel. The nonmetal can be silicon oxide, glass or plastic. In one embodiment, the material of the substrate **126** is silicon oxide. The surface of the substrate **126** contacting the graphene film **124** is planar.

The graphene film **124** can be fabricated by chemical vapor deposition method, mechanical pressing method, or tearing from oriented graphite using a tape.

In one embodiment, the graphene film **124** is made by the mechanical pressing method. The mechanical pressing method includes:

N**1**, providing a graphite block, and cutting the graphite block to form a clean cleavage surface thereon;

N**2**, disposing the graphite block having the clean cleavage surface thereon on the substrate **126**, wherein the cleavage surface is in contact with the substrate **126**;

N**3**, applying a pressure on the graphite block for a predetermined period of time; and

N**4**, removing the graphite block from the substrate **126** to form a graphene film **124** on the substrate **126**.

In the step N**1**, the graphite block can be highly oriented pyrolytic graphite or natural flake graphite.

In the step N**3**, the pressure can be in a range from about 98 Pa to about 196 Pa. The pressure can be applied for about 5 minutes to about 10 minutes. The graphite has a laminar cleavage structure. The cleavage surface of the graphite has a poor molecular attraction. Thus, the graphene can be easily peeled off along the cleavage surface of the graphite under the pressure.

The graphene film **124** formed by the mechanical pressing method is a complete and continuous graphene sheet.

In the step M**2**, the plastic support film **122** and the graphene film **124** disposed on the surface of the substrate **126** are overlapped with each other to form a laminar structure. In the laminar structure, the plastic support film **122** is in contact with the graphene film **124**. In one embodiment, the plastic support film **122**, the graphene film **124** and the substrate **126** are combined by pressing the laminar structure under a pressure to form the SGPC **128**. In the SGPC **128**, the graphene film **124** and the plastic support film **122** are closely combined by intermolecular forces under the pressure. In another embodiment, the plastic support film **122** and the graphene film **124** are directly adhered to each other to form the SGPC **128**.

In the step M3, the substrate **126** can be removed by solution corrosion method or etching method. In one embodiment, the substrate **126** is removed by solution corrosion method. The solution corrosion method includes the following steps: providing a NaOH solution; immersing the SGPC **128** in the NaOH solution to corrode the substrate **126** composed of silicon oxide, thereby forming a graphene-plastic support film composite structure; taking out the graphene-plastic support film composite structure from the NaOH solution; cleaning the graphene-plastic support film composite structure using deionized water; and drying the graphene-plastic support film composite structure, thereby forming the current collector **12**.

Referring to FIG. **6**, in one embodiment, an electrochemical cell electrode **10** using the current collector **12** is provided. The electrochemical cell electrode **10** includes the current collector **12** and an electrode material layer **14** covering on at least one surface of the current collector **12**.

The electrode material layer **14** can be covered on the graphene film **124** disposing on two opposite surfaces of the current collector **12** along a thickness direction of the current collector **12**. The electrode material layer **14** includes electrode active material, conductive agent and adhesive. The electrode active material, conductive agent and adhesive are uniformly mixed. The conductive agent in the electrode material layer **14** can be carbon fiber, acetylene black or carbon nanotube. The adhesive can be polyvinylidene fluoride, polytetrafluoroethylene, or styrene-butadiene rubber. The electrode active material can be a cathode active material or anode active material commonly used in the current electrochemical battery. The cathode active material can be doped or undoped spinel lithium manganese oxide, layered lithium manganese oxide, lithium nickel oxide, lithium cobalt oxide, lithium iron phosphate, lithium nickel manganese oxide, lithium nickel cobalt oxide, or any combination thereof. The anode active material can be natural graphite, organic cracking carbon, mesocarbon microbeads, or any combination thereof. The electrode material layer **14** can be firmly combined with graphene film **124** via the adhesive in the electrode material layer **14**.

Referring to FIG. **7**, in one embodiment, an electrochemical cell **20** is provided. The electrochemical cell **20** includes a cathode **22**, an anode **24**, a separator **26**, and a nonaqueous electrolyte solution **28**. The cathode **22** and the anode **24** are stacked with each other and sandwich the separator **26**. The cathode **22** includes cathode current collector **222** and cathode material layer **224** formed on the surface of the cathode current collector **222**. The anode **24** includes anode current collector **242** and anode material layer **244** formed on the surface of the anode current collector **242**. The anode material layer **244** and the cathode material layer **224** are opposite to each other and separated by the separator **26**. At least one of the cathode current collector **222** and the anode current collector **242** can use the above current collector **12**.

The electrochemical cell **20** can further include an exterior encapsulating structure, such as a hard battery case **29** sealed by a sealing member **30**, or a soft encapsulating bag, having the cathode **22**, the anode **24**, the separator **26** and the electrolyte solution **28** located therein.

In the electrochemical cell **20**, the plastic support film **122** and the graphene film **124** in the current collector **12** have a small density and excellent corrosion resistance, thereby decreasing the weight and increasing the life of the electrochemical cell **20**. In addition, the graphene film **124** has an

excellent conductive and directly contacts the electrode material layer **14**, thereby decreasing a contact resistance between the current collector **12** and the electrode material layer **14**.

Furthermore, the electrochemical cell electrode **10** can be used in current different electrochemical cells, such as lithium ion battery, supercapacitor or nickel-cadmium battery.

EXAMPLE

In an exemplary embodiment of the lithium ion battery, the material of the plastic support film **122** of the current collector **12** in cathode is polyethylene. A thickness of the graphene film is about 100 nm. The cathode material layer is composed of lithium iron phosphate, conductive agent and adhesive mixed with each other. The mass percentage of the lithium iron phosphate is in a range from about 85% to about 98%. The mass percentage of the conductive agent is in a range from about 1% to about 10%. The mass percentage of the adhesive is in a range from about 1% to about 5%. The material of the anode is lithium metal. The electrolyte is formed by dissolving the lithium hexafluorophosphate ($LiPF_6$) in a solvent composed of ethylene carbonate (EC) and carbonic acid methyl ethyl ester (EMC). A molar concentration of the $LiPF_6$ is 1 mol/L. A volume ratio of EC to EMC is 1:1. FIG. **8** shows voltage-capacity curves in charge and discharge processes of the lithium ion battery. The lithium ion battery is charged to 3 V using a constant current of 2.5 mA, and then discharged to 1 V using the constant current of 2.5 mA. FIG. **9** shows a voltage-time curve in charge and discharge cycling processes of the lithium ion battery, the lithium ion battery is charged to 3 V using the constant current of 2.5 mA, and then discharged to 1 V using the constant current of 2.5 mA, the charge and discharge processes are repeatedly executed. According to FIG. **8** and FIG. **9**, the lithium ion cell can be repeatedly charged or discharged for many times.

Depending on the embodiment, certain steps of methods described may be removed, others may be added, and the sequence of steps may be altered. It is also to be understood that the description and the claims drawn to a method may include some indication in reference to certain steps. However, the indication used is only to be viewed for identification purposes and not as a suggestion as to an order for the steps.

Finally, it is to be understood that the above-described embodiments are intended to illustrate rather than limit the present disclosure. Variations may be made to the embodiments without departing from the spirit of the present disclosure as claimed. Elements associated with any of the above embodiments are envisioned to be associated with any other embodiments. The above-described embodiments illustrate the scope of the present disclosure but do not restrict the scope of the present disclosure.

What is claimed is:

1. A method for making an electrochemical cell comprising:

making a current collector of the electrochemical cell comprising:

providing a substrate, a graphene film, and a plastic support film, wherein the substrate has a surface, the plastic support film is resistive to a corrosion of an electrolyte solution of the electrochemical cell, and the graphene film is disposed on the surface of the substrate;

laminating the graphene film disposed on the surface of the substrate and the plastic support film to form a substrate-graphene-plastic support film composite structure; and removing the substrate by a solution corrosion method or an etching method, wherein the current collector comprises the plastic support film and the graphene film coated on the plastic support film; and

preparing an electrochemical cell electrode by covering an electrode material layer on the graphene film of the current collector;

wherein the graphene film is fabricated by a mechanical pressing method, and the mechanical pressing method comprises:

providing a graphite block, and cutting the graphite block to form a clean cleavage surface thereon;

disposing the graphite block having the clean cleavage surface thereon on the substrate,

wherein the cleavage surface is in contact with the substrate;

applying a pressure on the graphite block for a predetermined period of time; and

removing the graphite block from the substrate to form the graphene film on the substrate.

2. The method as claimed in claim **1**, wherein the laminating the graphene film disposed on the surface of the substrate and the plastic support film comprises:

overlapping the graphene film disposed on the surface of the substrate and the plastic support film, wherein the graphene film is in contact with the plastic support film; and

pressing the graphene film disposed on the surface of the substrate and the plastic support film by another pressure.

3. The method as claimed in claim **1**, wherein the laminating the graphene film disposed on the surface of the substrate and the plastic support film comprises directly adhering the plastic support film to the graphene film.

4. The method as claimed in claim **1**, wherein the pressure is in a range from about 98 Pa to about 196 Pa.

5. The method as claimed in claim **4**, wherein the pressure is applied for about 5 minutes to about 10 minutes.

6. The method as claimed in claim **1**, wherein a material of the substrate is silicon oxide.

7. The method as claimed in claim **2**, wherein the graphene film and the plastic support film are combined by intermolecular forces in the substrate-graphene-plastic support film composite structure.

8. The method as claimed in claim **1**, wherein the graphene film is a continuous and integrated graphene sheet.

9. The method as claimed in claim **1**, wherein the plastic support film is a sheet shaped film, network shaped film, or porous shaped film.

10. The method as claimed in claim **1**, wherein a material of the plastic support film is selected from the group consisting of polyethylene, polypropylene, polyvinyl chloride, polystyrene, acrylonitrile-butadiene-styrene common polymer and combination thereof.

11. The method as claimed in claim **1**, wherein a thickness of the plastic support film is in a range from about 1 μm to about 200 μm.

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